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PAPER


# Development of an ombrotrophic peat bog (low ash) reference material for the determination of elemental concentrations†

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Given the increasing interest in using peat bogs as archives of atmospheric metal deposition, the lack of validated sample preparation methods and suitable certified reference materials has hindered not only the quality assurance of the generated analytical data but also the interpretation and comparison of peat core metal profiles from different laboratories in the international community. Reference materials play an important role in the evaluation of the accuracy of analytical results and are essential parts of good laboratory practice. An ombrotrophic peat bog reference material has been developed by 14 laboratories from nine countries in an inter-laboratory comparison between February and October 2002. The material has been characterised for both acid-extractable and total concentrations of a range of elements, including Al, As, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, P, Pb, Ti, V and Zn. The steps involved in the production of the reference material (*i.e.* collection and preparation, homogeneity and stability studies, and certification) are described in detail.

## Introduction

Environmental samples such as tree rings, mosses, aquatic sediments, snow, ice, and peat have been used as archives for the study of atmospheric metal deposition.[1–3] The surface layers in ombrotrophic raised bogs are isolated from the influence of local ground water and surface water, and receive their inorganic content by atmospheric deposition only.[4] Ombrotrophic peat that has accumulated during the past hundreds or thousands of years, therefore, can be used to study vegetation history, climate change, and, in principle, the historical trend of atmospheric metal deposition. Most recent

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relevant research results,[5–9] *e.g.* for Pb, have been consistent with information from other archives, including lake sediments and ice cores, and are compatible with known historical trends where available, *e.g.* the emission of Pb from different sources. Given the increase in this type of study, the lack of a common, validated sample preparation method and of a certified peat reference material has hindered not only the quality assurance of the generated analytical data but also the interpretation and comparison of peat core metal profiles from different laboratories in the international community. Instead of using an authentic peat reference material, quality control in this sort of study has long been referred to certified reference materials (CRMs) developed for plants and soils. Although an attempt, as yet uncompleted, was made to develop a peat reference material for quality control use by laboratories in the international peat bog community,[10] the material was of fen origin and had high ash content ($\sim$20%), uncharacteristic of ombrotrophic peat bogs. In addition, different laboratories in this field of research currently adopt a wide range of practices, including the determination of acid-extractable and of total elemental concentrations by various instrumental analytical techniques. To compare and standardise these different approaches, we developed a new candidate peat reference material, derived from an ombrotrophic bog, and subjected it to an international inter-laboratory study as part of the certification process.

The total concentrations of elements can be determined by using non-destructive analytical techniques (XRF, INAA, *etc.*) or destructive analytical techniques employing ashing procedures, such as mixtures of mineral acids with HF for wet ashing or dissolution after dry ashing, alkaline fusion *etc.*, followed by AAS, ICP-OES, ICP-MS *etc.* The acid-extractable concentrations of elements are conventionally defined by the procedures involving extraction with aqua regia, boiling 2 M $HNO_3$, or cold 2 M $HNO_3$.[11] Reference materials characterised for both acid-extractable and total concentrations of elements are of value to laboratories that cannot or do not employ HF to achieve total dissolution of aluminosilicate minerals in sample matrices.

## Methods

### Collection and preparation of the candidate ombrotrophic peat reference material

On 11 September, 2001, the starting material was collected from the ombrotrophic peat bog at Flanders Moss, near Stirling, Scotland. Vegetation on top of the bog was removed using a stainless steel knife and the peat sample dug up by a spade from a depth of $\sim$30 cm in blocks of approximate size 20 cm $\times$ 20 cm $\times$ 30 cm. Seven blocks of peat of about the same size were collected, yielding a total wet weight of $\sim$70 kg. The wet peat was wrapped up in a polyethylene bag and transported to the Macaulay Institute, Aberdeen, UK, the following day. It was then divided into sub-samples, from which root material was extracted by hand, and air-dried at 30 °C for 10 days on paper-lined aluminium trays. The dried peat was then broken into small aggregates with a wooden hammer and air-dried for a further week. Ten sub-samples were then randomly taken from the drying trays. The moisture content based on oven-drying at 105 °C was determined on each sub-sample, yielding a mean moisture content of $\sim$10% in 30 °C air-dried peat. The air-dried peat was milled to less than 2 mm in particle size with a stainless steel hammer mill (Christie Hunt). Approximately 4.5 kg of peat material was obtained and transferred into a 20-litre glass jar, which was placed on a roller bed for two weeks.

### Preliminary study of homogeneity

Ten sub-samples ($\sim$2 g each) were randomly taken from the jar and analysed for metal concentrations to make a preliminary assessment of the bulk homogeneity using a modified version of ASTM 826-85 "Standard practice for testing homogeneity of material for development of reference material".[12] This mainly involved the selection of test sub-samples from the bulk material, digestion and analysis of sub-samples (0.25 g), and statistical treatment of the measurement data using the ASTM 826-85 standard protocol. The total concentration for each element of interest was the variable we evaluated to assess homogeneity. The USEPA Method 3052 Protocol[13] was modified for the digestion of sub-samples, carried out by microwave-assisted HF–$HNO_3$ digestion of peat (total-total digestion method). This method consisted of a representative sample of up to 0.25 g (the initial weight) being ashed at 450 °C for 4 h prior to digestion in 9 ml of concentrated $HNO_3$ and 0.5 ml HF for about 15 minutes using microwave heating with a suitable laboratory microwave system. The sample and acid are placed in suitably inert polymeric microwave vessels. The vessel is sealed and heated in the microwave system. The temperature profile is specified to permit specific reactions and incorporates reaching 180 $\pm$ 5 °C in $\sim$5.5 minutes and remaining at 180 $\pm$ 5 °C for 9.5 minutes for the completion of specific reactions. After cooling, the vessel contents are filtered, evaporated to $\sim$1 ml, and then diluted to volume and analysed by FAAS, GFAAS, ICP-OES, or ICP-MS.

Following the preliminary homogeneity tests, the peat material was further homogenised by mixing in the jar on the roller bed for another week. The roller bed was then stopped, and peat material was taken from the jar to fill a series of five pre-cleaned amber glass bottles, each containing a minimum of 30 g. After that, they were promptly closed using polyethylene screwcaps. The glass jar was again rotated for another five minutes and the next five bottles were filled in the same way. The cycle was repeated until a total of 145 (29 $\times$ 5) bottles of candidate peat reference material were finally obtained. About ten percent of the bulk peat material that was left on the bottom of the jar was discarded, just in case it was less homogeneous.[14,15] Twenty-nine bottles (one from each series) were set aside for homogeneity and stability testing. The candidate ombrotrophic peat bog reference material was then named NIMT/UOE/FM/001. The ash content (450 °C) of this material was $\sim$4–5% of the 30 °C air-dried weight.

### Homogeneity testing

Homogeneity testing for total and acid-extractable concentrations of elements in the candidate ombrotrophic peat bog reference material was carried out by using the *F*-test and ANOVA statistical test. Sixteen (three times the cube root of *n* units)[16] bottles of candidate peat bog reference material were randomly selected from the 29 bottles that had been set aside earlier. As before, microwave-assisted HF–$HNO_3$ digestion of peat (total–total digestion method), a modification of the USEPA Method 3052 Protocol, was utilised for total element concentration, while microwave-assisted $HNO_3$ digestion of peat (total–extractable digestion method), a modification of the USEPA Method 3051 Protocol,[17] yielded acid-extractable element concentration. The latter digestion method employs 10 ml of $HNO_3$ as reagent instead of the $HNO_3$–HF mixture used in the former.

### Stability study

The stability of the candidate peat bog reference material was tested by storing bottles of the candidate reference material at $-20$ °C, $+4$ °C, $+20$ °C, and $+40$ °C for a period of 12 months. After 1, 3, 6 and 12 months, the total and acid-extractable elemental concentrations were determined (in five replicates). The procedures were the same as those used in the homogeneity study. Instability would be detected by comparing the

measured element concentrations of samples stored at +4 °C, +20 °C, +40 °C with those of samples stored at −20 °C as determined at various times over 12 months. The samples stored at −20 °C were used as reference for the samples stored at +4 °C, +20 °C and +40 °C, respectively.

### Certification of concentration

An international inter-laboratory comparison exercise was conducted to certify the reference material. Laboratories invited to take part in the certification exercise were those of experienced research groups in this field of study, considered to be well-equipped and employing quality control and quality assurance procedures. The 14 laboratories taking part were requested to verify the quality of their measurements, in particular, the validity of calibration (including calibration of balances, volumetric glasswares and other tools of relevance). Participants were free to choose analytical methods of which they had previous experience and could therefore be expected to give valid results when applied by an experienced analyst. They were also asked to make a minimum of five independent replicate determinations of each element in the candidate reference material, each laboratory being supplied with one bottle of prepared peat material.

On receipt of data from participants, an identification number (Laboratory ID) was assigned to each laboratory. Where there were two separate sets of data, *i.e.* one for total elemental concentration and another for acid-extractable element concentration, the Laboratory ID for the latter set is not necessarily the same as that for the former set. Nine laboratories reported data for total ($HNO_3$–HF, $HNO_3$–$HBF_4$, $HNO_3$–$H_2O_2$–$H_2O$–HF) concentrations, and ten laboratories for acid-extractable ($HNO_3$, $HNO_3$–HCl, $HNO_3$–$HClO_4$) concentrations, using a range of digestion conditions and a variety of analytical techniques (AAS, GFAAS, ICP-OES, ICP-MS), including, in the case of one laboratory, XRF analysis of the solid phase, and, in two others, thermal decomposition AAS for Hg. Table 1 lists the digestion methods and instrumental analytical techniques used by the participants.

## Results and discussion

### Preliminary study of homogeneity

Using Pb as an example, the measurement results (Table 2) were treated as follows:

$T$, $B$, $t'$, and $G$ were computed, where: $T$ = sum of each column; $B$ = sum of each row; $t'$ = mean of each column; and $G$ = sum of $B_1 \ldots B_n$; $b$ = number of replicate measurements from different aliquots of the solid material (3); and $t$ = number of sub-samples (10)

The degree of freedom at 95% confidence level was calculated from:

$v = (b - 1)(t - 1)$, where $v$ = the number of degrees of freedom

$v = 18$

The value of symbol $q$ corresponding to $t$ and $v$ was found from the reference table given in ASTM 826-85.[12]

$q = 5.07$

The sum of squares due to the sub-samples, $S_t$, was calculated from

$S_t = [(T_1^2 + T_2^2 + \ldots T_t^2)/b] - (G^2/tb) = 341$

The sum of squares due to runs, $S_b$, was calculated from

$S_b = [(B_1^2 + B_2^2 + \ldots B_t^2)/t] - (G^2/tb) = 69$

**Table 1** Digestion methods and instrumental analytical techniques used by participants in the inter-laboratory comparison exercise for elemental concentrations in NIMT/UOE/FM/001

| Methodologies | |
|---|---|
| **Total concentration** | **Acid-extractable concentration** |
| **Lab1**: $HNO_3$–$HBF_4$ high pressure microwave autoclave, ICP-MS | **Lab1**: $HNO_3$ microwave-assisted, ICP-OES |
| **Lab2**: $HNO_3$–$H_2O_2$–$H_2O$–HF microwave-assisted, ICP-OES | **Lab2**: $HNO_3$ microwave-assisted, HR-ICP-MS |
| **Lab3**: $HNO_3$–HF pressure digestion, ICP-MS | **Lab3**: $HNO_3$ high-pressure ashing, ICP-MS, HG-AAS (for As) |
| **Lab4**: XRF | **Lab4**: $HNO_3$ microwave-assisted (USEPA Method 3051 Protocol), ICP-OES, GFAAS |
| **Lab5**: $HNO_3$–HF total digestion, ICP-OES | **Lab5**: aqua regia reflux digestion, ICP-OES |
| **Lab6**: $HNO_3$–HF microwave-assisted (USEPA Method 3052 Protocol), ICP-OES, GFAAS | **Lab6**: $HNO_3$ microwave-assisted (USEPA Method 3051 Protocol), GFAAS, ICP-OES; $HNO_3/H_2SO_4$ digestion @60 °C, 2 h, CVAAS (for Hg only) |
| **Lab7**: $HNO_3$–HF microwave-assisted (USEPA Method 3052 Protocol), ICP-MS | **Lab7**: aqua regia digestion RT 24 h, 100 °C, 1 h, ICP-MS, ICP-OES |
| **Lab8**: thermal decomposition AAS (for Hg only) | **Lab8**: aqua regia digestion @125 °C, 3 h, FAAS |
| **Lab9**: thermal decomposition AAS (for Hg only) | **Lab9**: $HNO_3$–$HClO_4$, heating, ICP-OES |
| | **Lab10**: $HNO_3$ microwave-assisted (USEPA Method 3051 Protocol), ICP-MS |

The laboratory ID numbers in the total concentration column (and in Figs. 1 and 2) do not necessarily correspond to those in the acid-extractable concentration column (and in Figs. 3 and 4).

**Table 2** Data for total Pb concentration (mg $kg^{-1}$) (dry-weight (105 °C) basis, *i.e.* corrected for moisture content of the air-dried peat) in the preliminary homogeneity testing of the candidate ombrotrophic peat (low ash) reference material

| | Sub-sample numbers | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Replicate | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | Total |
| **1** | 154 | 172 | 168 | 164 | 164 | 170 | 165 | 174 | 164 | 175 | $B_1$ = **1672** |
| **2** | 175 | 188 | 169 | 163 | 164 | 169 | 163 | 172 | 163 | 180 | $B_2$ = **1705** |
| **3** | 173 | 168 | 169 | 165 | 172 | 162 | 178 | 164 | 185 | 166 | $B_3$ = **1703** |
| Total | $T_1$ = **501** | $T_2$ = **528** | $T_3$ = **506** | $T_4$ = **493** | $T_5$ = **500** | $T_6$ = **501** | $T_7$ = **507** | $T_8$ = **511** | $T_9$ = **512** | $T_{10}$ = **521** | $G$ = **5080** |
| Mean | $t'_1$ = **167** | $t'_2$ = **176** | $t'_3$ = **169** | $t'_4$ = **164** | $t'_5$ = **167** | $t'_6$ = **167** | $t'_7$ = **169** | $t'_8$ = **170** | $t'_9$ = **171** | $t'_{10}$ = **174** | |

The sum of squares of all the measurements in Table 2, $S_{\text{average}}$, was defined and calculated from

$$S_{\text{average}} = \left(\sum_{i=1}^{t}\right)\left(\sum_{j=1}^{b}\right) Y_{ij}^2 - \left(G^2/tb\right)$$

where $Y_{ij}$ = individual values in Table 2.

$S_{\text{average}} = 1491$

The symbol $s$ was defined and calculated from

$$s = \sqrt{\left(S_{\text{average}} - S_{\text{b}} - S_{\text{t}}\right)/(b-1)(t-1)} = 7.8$$

The symbol $w$ was defined and calculated from

$$w = qs/\sqrt{b} = 23$$

The maximum and minimum of the mean $t'$ values in Table 2 are 176 and 164, respectively, so the maximum difference between any of the mean $t'$ values in Table 2 is 12. As the absolute difference between any two mean values does not exceed $w$ (=23), then there is strong evidence, at 95% confidence level, that the bulk material is homogeneous for Pb. The same treatment was applied to Al, Ca, Co, Cu, Fe, Mg, Mn, Ti, V, and Zn for which similar satisfactory evidence of homogeneity was obtained in each case.

## Homogeneity testing

Analytical results for total Pb concentration, expressed in mg $kg^{-1}$ on a dry-weight (at 105 °C) basis, are given in Table 3. Using Microsoft Excel™, Table 4 displays the associated ANOVA calculation (one-way layout), in which *SS* provides the sum of squares, *df* represents the associated degrees of freedom, and *MS* expresses mean squares, which form the basis for the computation of variation. The *P-value* gives the level for which the calculated $F$ ($F_{\text{cal}}$) equals $F_{\text{critical}}$. From Table 4, where it can be seen that $F_{\text{cal}}$ does not exceed $F_{\text{critical}}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Pb concentration. The same treatment was applied to other elements of interest, in each case demonstrating the homogeneity of the candidate material. On the basis of these results, the material was considered to be homogeneous at the level of 0.25 g, the typical 30 °C air-dried weight taken for analysis.

## Stability study

The ratios ($R_{\text{T}}$) of the mean values ($\bar{X}_{\text{T}}$) of five replicate measurements made for samples stored at +4 °C, +20 °C and +40 °C and the mean value ($\bar{X}_{-20\,^{\circ}\text{C}}$) from the five determinations at −20 °C were calculated as:

$$R_{\text{T}} = \bar{X}_{\text{T}}/\bar{X}_{-20\,^{\circ}\text{C}}$$

**Table 4** Analysis of variance (ANOVA) for homogeneity testing of total Pb concentration (mg $kg^{-1}$) in the candidate ombrotrophic peat (low ash) reference material

| Source of variation | *SS* | *df* | *MS* | $F_{\text{cal}}$ | *P-value* | $F_{\text{critical}}$ |
|---|---|---|---|---|---|---|
| **Between bottles** | 575 | 15 | 38 | 1.559 | 0.142 | 1.992 |
| **Within bottles** | 787 | 32 | 25 | | | |
| **Total** | 1362 | 47 | | | | |

The uncertainty $U_{\text{T}}$ was obtained from the coefficient of variation (CV) of five measurements obtained at each temperature: $U_{\text{T}} = \left(CV_{\text{T}}^2 + CV_{-20\,^{\circ}\text{C}}^2\right)^{1/2} R_{\text{T}}$

The $R_{\text{T}}$ ratio should be 1 in the case of ideal stability but, as slight instability might be expected during long storage times, the value 1 should lie between $R_{\text{T}} - U_{\text{T}}$ and $R_{\text{T}} + U_{\text{T}}$. For greater than 98% of the measurements made for samples stored at these conditions, the values fell within $R_{\text{T}} \pm U_{\text{T}}$. It was concluded that there was no instability for a storage time of one year under these conditions. As the candidate material is stable under the storage condition of +40 °C for one year, it can be assumed that the material may be stable for up to two or three years under the storage condition of +20 °C or below. As a result of the stability testing, all of the elements determined were considered to be suitable for certification, provided that the material is stored at typical room temperature or under refrigeration.

## Certification of concentration

The sets of results submitted by participants were assumed to be normally distributed, and analysed statistically[16,18] using Grubbs and Cochran's tests to detect outlying values. The Grubbs test[16,18] was used to detect outlying values in the population of individual results and in the population of laboratory means, while Cochran's test[16,18] was used to identify outlying values in the laboratory variances. A summary of the statistical evaluation is given in the certification report.

Using the certification of the total Pb concentration as an example, seven laboratories (1, 2, 3, 4, 5, 6, 7) submitted data for total Pb concentration. The Laboratory Means, standard deviation, and 95% confidence interval of the data from each laboratory are shown in Fig. 1a. The individual replicate results from each laboratory were tested for outliers by using Grubbs 1, Grubbs 2, and Grubbs 3 tests. One replicate from

**Table 3** Data for total Pb concentration (mg $kg^{-1}$) (dry-weight (105 °C) basis, *i.e.* corrected for moisture content of the air-dried peat) in the homogeneity testing of the candidate ombrotrophic peat (low ash) reference material

| | Concentration/mg $kg^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| Sample | Replicate #1 | Replicate #2 | Replicate #3 | Mean | Variance | *n* |
| **#1** | 163 | 162 | 157 | 160 | 10.1 | 3 |
| **#2** | 162 | 160 | 161 | 161 | 0.8 | 3 |
| **#3** | 165 | 159 | 166 | 164 | 12.8 | 3 |
| **#4** | 165 | 158 | 159 | 161 | 17.1 | 3 |
| **#5** | 152 | 159 | 166 | 159 | 48.3 | 3 |
| **#6** | 159 | 166 | 161 | 162 | 10.2 | 3 |
| **#7** | 164 | 165 | 164 | 164 | 0.3 | 3 |
| **#8** | 165 | 162 | 165 | 164 | 3.2 | 3 |
| **#9** | 157 | 156 | 169 | 161 | 47.2 | 3 |
| **#10** | 164 | 163 | 161 | 163 | 2.6 | 3 |
| **#11** | 160 | 152 | 147 | 153 | 41.4 | 3 |
| **#12** | 158 | 154 | 148 | 153 | 27.6 | 3 |
| **#13** | 168 | 161 | 166 | 165 | 12.0 | 3 |
| **#14** | 162 | 165 | 166 | 164 | 4.2 | 3 |
| **#15** | 169 | 170 | 154 | 164 | 79.9 | 3 |
| **#16** | 154 | 154 | 169 | 159 | 75.8 | 3 |

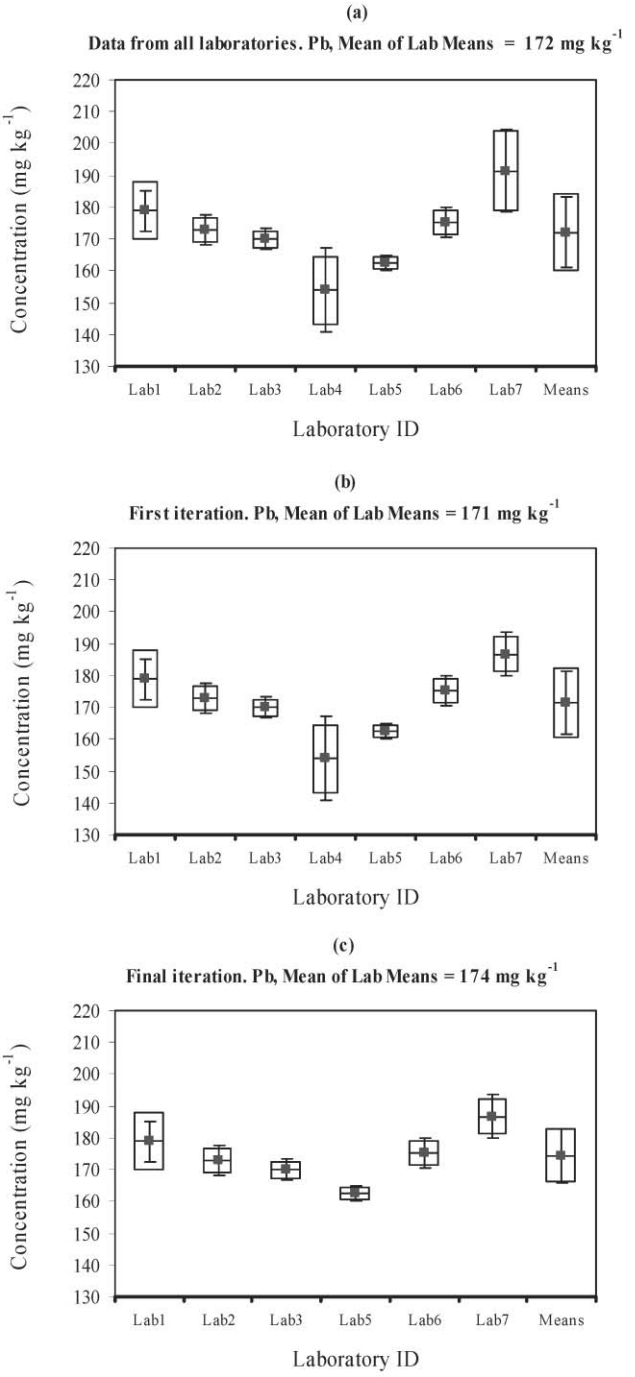


**Fig. 1** Inter-laboratory comparison results for total Pb concentration (expressed as concentration, mg $kg^{-1}$, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (□□).

Laboratory 7 was identified as a Grubbs 1 outlier. The outlier was then removed, with the resulting outcome for Laboratory 7 shown in Fig. 1b. The Laboratory Means of data from each laboratory were then tested for possible Grubbs 1, Grubbs 2, Grubbs 3, and Cochran's outliers. No Grubbs outlier was identified but it was decided to reject the Laboratory Mean from Laboratory 4 as a Cochran's outlier (variance outlying), evaluation of the data at this stage being displayed in Fig. 1c. Although the Laboratory Mean from Laboratory 1 could perhaps have been rejected as a Cochran's outlier (variance outlying), it was decided to retain it as the spread of results from the six laboratories was considered acceptable. The data processing was therefore stopped at this stage, with a mean Pb concentration of 174 mg $kg^{-1}$.

The sets of results accepted on technical and statistical grounds are presented in Figs. 2–4. Fig. 2 displays the calculated mean, standard deviation and 95% confidence interval (CI) of the accepted inter-laboratory comparison results for total Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn concentrations (expressed as concentration, mg $kg^{-1}$, corrected for moisture content), after the final iteration. For acid-extractable concentrations (expressed as concentration, mg $kg^{-1}$, corrected for moisture content), the calculated mean, standard deviation and 95% confidence interval of the accepted inter-laboratory comparison results after the final iteration are shown for As, Cd, Co, Cr, Cu, Mn, Ni, Pb V, and Zn in Fig. 3 and for Al, Fe, Mg and P in Fig. 4.

### Calculation of uncertainty

Again using Pb as the example, the uncertainty of the value assigned to the total Pb concentration (174 mg $kg^{-1}$) of the ombrotrophic peat bog certified reference material was calculated according to a modification of the Guide on the Expression of Uncertainty in Measurement[19–24] (GUM), using the equation: $U_{CRM} = k\sqrt{u_{char}^2 + u_{bb}^2}$ where $U_{CRM}$ = expanded uncertainty of the total Pb concentration of the peat bog certified reference material; $k$ = coverage factor; $u_{char}$ = uncertainty of the certified metal concentration in the ombrotrophic peat bog reference material; $u_{bb}$ = uncertainty of the between-bottle inhomogeneity. The uncertainty of the instability ($u_{stab}$) was not included in view of the previously demonstrated stability and in accordance with criteria for the production of a quality control reference material.[16]

As we do not have the full uncertainty budget from the participants in the inter-laboratory comparison exercise, $u_{char}$ can be calculated from the equation: $u_{char} = \frac{s}{\sqrt{l}}$ where $s$ = standard deviation of laboratory means, *i.e.* 8 mg $kg^{-1}$; $l$ = number of laboratories, *i.e.* 6. Therefore, $u_{char}$ = 3.27 mg $kg^{-1}$, *i.e.* 1.88% of 174.

The value of $u_{bb}$ can be estimated from ANOVA of the data from homogeneity testing as: $u_{bb} = \sqrt{\frac{MS_{among} - MS_{within}}{n}}$ where $MS_{among}$ = mean square among units, *i.e.* 38; $MS_{within}$ = mean square within units, *i.e.* 25; $n$ = number of subsamples per unit, *i.e.* 3. Therefore, $u_{bb}$ = 2 mg $kg^{-1}$, *i.e.* 1.29% of 174.

The expanded uncertainty of the value assigned to the total Pb concentration (174 mg $kg^{-1}$) in the ombrotrophic peat bog certified reference material can be calculated from: $U_{CRM} = ku_c$ where $u_c = \sqrt{u_{char}^2 + u_{bb}^2}$, *i.e.* 2.28%. Therefore, $U_{CRM}$ ($k$ = 2) = 4.56% of 174.

Therefore the certified value for total Pb concentration in the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001 is 174 ± 8 mg $kg^{-1}$.

### Certified and information-only values

By applying the same treatment as for Pb to the other inter-laboratory comparison results, the certified values (coverage factor of 2) for all inorganic elements determined in the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001 were calculated and are displayed in Table 5. Where concentration data were not sufficient and considered too variable, the arithmetic means (±1 SD) are given as information-only values for some elements.

The acid-extractable concentrations of Cd, Pb, and Zn are similar to their corresponding total concentrations (Table 5), whereas the acid-extractable concentration of Cr and of some major elements such as Al, Na, and Ti are clearly lower than their corresponding total concentrations. This suggests that Cr and these major elements occur in matrices that cannot

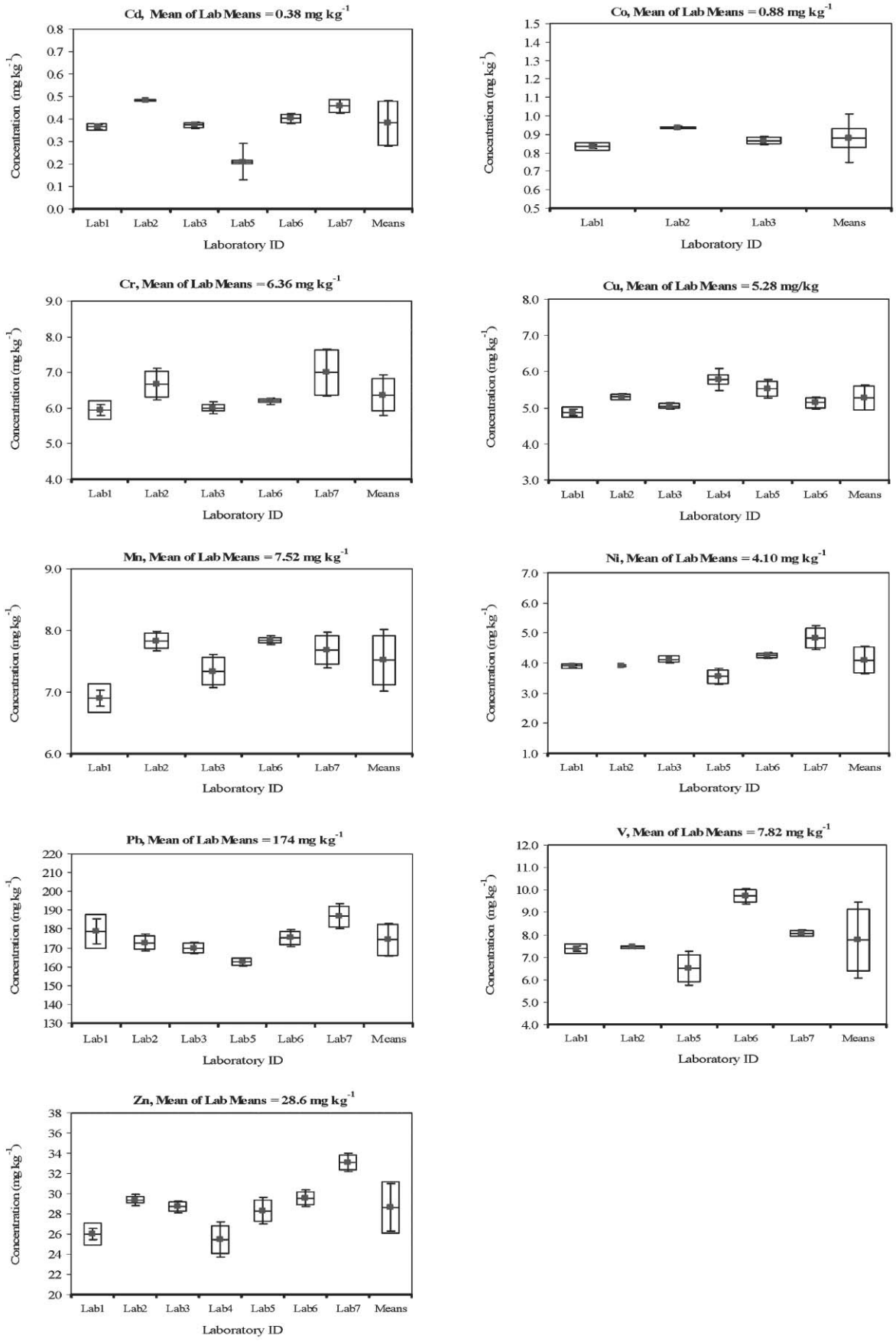


**Fig. 2** Inter-laboratory comparison results for total Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn concentrations (expressed as concentration, mg kg$^{-1}$, corrected for moisture content) of NIMT/UOE/FM/001, after final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊥).

be dissolved by conventional acid digestion methods. The employment of HF for wet digestion is needed in the study of Cr and some major elements. The variation of the acid-extractable results for some elements such as Al is probably a consequence of the range of digestion methods used by the participants.

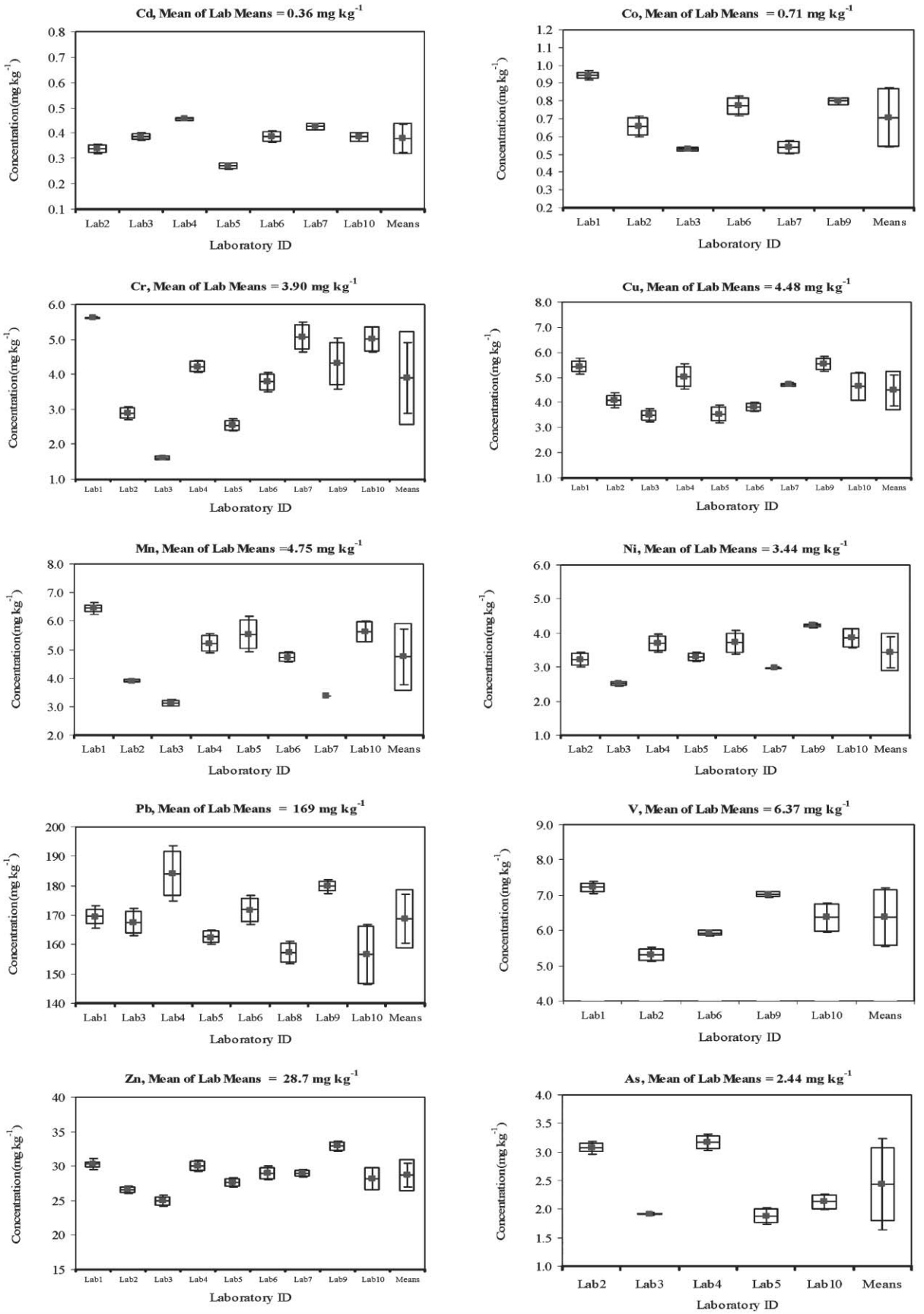


**Fig. 3** Inter-laboratory comparison results for acid-extractable As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn concentrations (expressed as concentration, mg $kg^{-1}$, corrected for moisture content) of NIMT/UOE/FM/001, after final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊥).

In addition to elemental concentration data, information on Pb isotopic composition was provided by three laboratories. Reported mean values of 1.1766 ± 0.0008, 1.1759 ± 0.0006, and 1.1765 ± 0.0003 yielded an overall information value of 1.1763 ± 0.0004 (±1 SD) for the $^{206}Pb/^{207}Pb$ ratio.

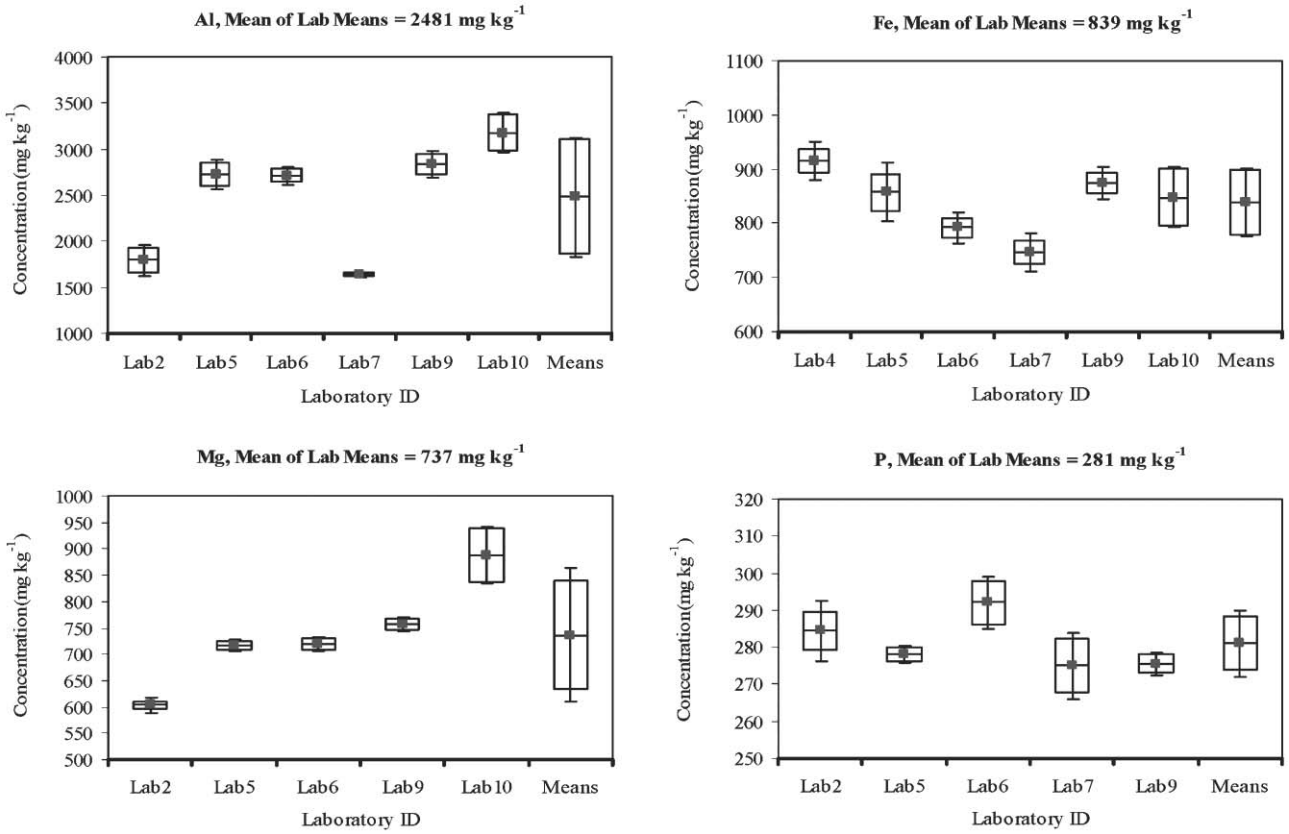


**Fig. 4** Inter-laboratory comparison results for acid-extractable Al, Fe, Mg, and P concentrations (expressed as concentration, mg $kg^{-1}$, corrected for moisture content) of NIMT/UOE/FM/001, after final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊥).

**Table 5** Certified values with uncertainties (coverage factor of 2) and information-only (italics) values [$\pm 1$ SD ($n \leqslant 4$)] for the elemental concentration of the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001

| | Certified values/mg $kg^{-1}$ | |
|---|---|---|
| Element ($x$, $y$)[a] | Total concentration[b] | Acid-extractable concentration[b] |
| Cd (6, 8) | 0.38 ± 0.08 (6) | 0.36 ± 0.05 (7) |
| Co (4, 6) | 0.88 ± 0.09 (3) | 0.71 ± 0.13 (6) |
| Cr (6, 9) | 6.36 ± 0.44 (5) | 3.90 ± 0.90 (9) |
| Cu (7, 10) | 5.28 ± 1.04 (6) | 4.48 ± 0.73 (9) |
| Fe (4, 8) | *921 ± 84 (4)* | 839 ± 54 (6) |
| Mn (6, 8) | 7.52 ± 0.41 (5) | 4.74 ± 0.87 (8) |
| Ni (7, 10) | 4.10 ± 0.37 (6) | 3.44 ± 0.40 (8) |
| Pb (7, 10) | 174 ± 8 (6) | 169 ± 8 (8) |
| V (5, 6) | 7.82 ± 1.08 (5) | 6.37 ± 0.73 (5) |
| Zn (7, 10) | 28.6 ± 1.9 (7) | 28.7 ± 1.6 (9) |
| As (4, 5) | *2.44 ± 0.55 (3)* | 2.44 ± 0.58 (5) |
| Hg (2, 2) | *0.169 ± 0.007 (2)* | *0.164 ± 0.020 (2)* |
| Al (3, 6) | *3692 ± 347 (3)* | 2481 ± 514 (6) |
| Ca (3, 4) | *683 ± 198 (3)* | *763 ± 172 (4)* |
| Mg (2, 5) | *582 ± 168 (2)* | 737 ± 95 (5) |
| Na (3, 3) | *817 ± 307 (3)* | *229 ± 78 (3)* |
| P (2, 5) | *265 ± 8 (2)* | 281 ± 7 (5) |
| Ti (3, 3) | *357 ± 18 (3)* | *110 ± 11(3)* |

[a] $x$ and $y$ indicate the number of laboratories that submitted results for total and acid-extractable elemental concentrations, respectively. [b] Under total and acid-extractable concentration, the number in brackets indicates the number of accepted laboratory results used in the certification exercise for each element.

### Applicability and availability

Although this ombrotrophic peat (low ash) reference material has been developed specifically for use in the analysis of ombrotrophic peat, it may also be of some value in the analysis of minerotrophic peat. Enquiries concerning the availability of the reference material NIMT/UOE/FM/001 for use by laboratories should be made to Dr. J. G. Farmer, University of Edinburgh, from whom instructions for use can also be obtained.

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